M^{III}N BASED MATERIALS AND METHODS AND APPARATUS FOR PRODUCING SAME

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Description

$M^{III}N$ BASED MATERIALS AND METHODS AND APPARATUS FOR PRODUCING SAME

Technical Field

The present invention is generally directed to the production of Group III metal nitride materials for use as free-standing articles as well as substrates for further processes and/or microelectronic and optoelectronic devices. In particular, the present invention is directed to the production of low-defect density, single-crystal materials and highly-oriented polycrystalline materials utilizing enhanced sputtering techniques.

Background

A wide variety of techniques exist for depositing thin films onto substrates in order to achieve desirable properties which are either different from, similar to, or superior to the properties of the substrates themselves. Thin films are employed in many kinds of optical, electrical, magnetic, chemical, mechanical and thermal applications. Optical applications include reflective/anti-reflective coatings, interference filters, memory storage in compact disc form, and waveguides. Electrical applications include insulating, conducting and semiconductor devices, as well as piezoelectric drivers. Magnetic applications include memory discs. Chemical applications include barriers to diffusion or alloying (e.g., galling), protection against oxidation or corrosion, and gas or liquid

sensors. Mechanical applications include tribological (wear-resistant) coatings, materials having desirable hardness or adhesion properties, and micromechanics. Thermal applications include barrier layers and heat sinks.

Bulk materials can be used as substrates upon which microelectronic and optical devices are fabricated. Wide bandgap semiconductor materials such as gallium nitride, aluminum nitride, indium nitride and their alloys are being studied for their potential application in microelectronics and opto-electronics. These materials are particularly well suited for short wavelength optical applications, such as green, blue and UV light emitting devices (LEDs and LDs), and visible and solar-blind UV detectors. The use of UV or blue GaN-based LEDs makes possible the fabrication of solid state white light sources, with higher efficiencies and lifetimes 10 to 100 times longer than conventional sources. Additionally, GaN has a region of negative differential mobility with a high peak electron velocity and high-saturated velocity, which can be used for fabricating high-speed switching and microwave components. P-type doping of GaN and AlGaN with relatively high hole concentrations is now readily achieved, and ohmic and Schottky contacts have been characterized for n- and p-type materials. Thus, many of the above devices have or potentially have large, technologically important markets. Such markets include display technology, optical storage technology, and space-based communications and detection systems. Other applications include high temperature microelectronics, opto-electronic devices, piezoelectric and acousto-optic modulators, negative-electron affinity devices and radiation/EMP hard devices for military and space uses.

Attempts to grow low-defect density gallium nitride (GaN) thin films heteroepitaxially on substrates such as sapphire and silicon carbide (SiC) have

had limited success. GaN materials heteroepitaxially grown on these substrates suffer from large concentrations of threading defects, typically on the order of $10^{-8} - 10^{-10}$ cm^{-2}, due to the large lattice mismatch between the film and substrate. Threading defects increase leakage currents in diode and FET structures and act as a significant source of noise in photodetectors. As a result, the operation of high performance devices, such as high-speed, high-sensitivity UV photodetectors, and high power, high frequency microelectronic devices, is presently limited. Buffer layers of AlN, GaN, and other materials have been used to reduce the lattice mismatch. However, threading defects and low angle grain boundaries remain in the films. Differences between the film and substrate thermal expansion coefficients also result in stresses in the films.

Accordingly, homoepitaxial growth of GaN thin films on bulk GaN substrates is of great interest. The use of GaN substrates would eliminate the problems due to lattice mismatch and thermal expansion mismatch. Unfortunately, the availability of GaN substrates has been limited due to conventional processing capabilities. This problem has hindered the development of devices based on GaN and related nitride semiconductors. Several obstacles exist to the successful manufacturing and commercializing of high device-quality Group III nitride-based materials, whether in bulk, single-crystal, polycrystalline or epitaxial form, for electronics and other applications. These obstacles generally include cost, reproducibility, and purity.

For instance, gallium nitride has a high equilibrium vapor pressure of nitrogen that results in its decomposition at elevated temperatures. The solubility of nitrogen in gallium metal at room temperature and pressure is very low. As a result, conventional crystal growth methods to produce GaN are not

practical. This has led to the development of several alternate bulk growth methods, including high-temperature, high-pressure (15 kbar) solution growth, evaporation, and sublimation.

Currently, aluminum nitride and gallium nitride exist only as polycrystalline or powder forms, or in thin films. Polycrystalline bulk aluminum nitride can be manufactured using powder processing techniques. This process has not yielded semiconductor-grade single crystal material. Formidable problems are associated with such techniques, beginning with the production of pure aluminum nitride powders and then the sintering of oxygen-free and defect-free aluminum nitride. Some of these problems include the production of both high-purity and uniform particle-size powders. The highest purity powders can contain up to 1% of oxygen and binders, such as Y_2O_3, that are needed to produce aluminum nitride with a high density. Therefore, high density is achievable at the expense of contamination. Sintering of these aluminum nitride powders is also a difficult process. The covalent nature of aluminum nitride prevents densification of pure aluminum nitride at low temperatures. Aluminum nitride decomposes at high temperatures, such as above 1600 ° C, thereby preventing densification. Hence, costly sintering aids such as high pressures and impurities are required for producing high-density material. Other problems associated with powder processing of aluminum nitride include maintaining the purity and integrity of the powder, controlling the environment at high sintering temperatures, and the production of defect-free parts. Aluminum nitride is very difficult to manufacture using powder processing techniques without introducing contamination that will have adverse effects on the optical and thermal properties of the material. These impurities can be present in the crystalline

lattice structure, and can migrate to the grain boundaries during sintering, causing the infrared absorbance to be high.

As disclosed hereinbelow, it has now been discovered that enhanced sputtering techniques, which are physical vapor deposition (PVD) techniques, can be feasibly utilized to produce low-defect density Group III metal nitride materials of bulk thickness and of device-quality crystal. Magnetron sputtering is traditionally associated with thin film deposition. An advantage of sputter synthesis is that high purity compounds can be formed directly from the high purity source materials. Moreover, the synthesis can be achieved under highly controlled conditions. Nitrogen and Group III metals such as aluminum are readily available, from multiple sources, in ultra-high purity grades (e.g., 99.9999%) for the microelectronics industry. Sputter synthesis is currently the process that most effectively eliminates hydrogen from the bulk, since the sputter environment is controllable to ultra-high vacuum conditions. Through sputter synthesis of Group III nitrides, it is possible to obtain materials that have properties near the bulk properties. Since this takes place under ultra-high vacuum conditions, hydrogen and oxygen can be eliminated from the material. Reactive sputtering has the advantage of producing high purity materials with high densities, and ease of fabrication of quality crystalline material.

However, traditional magnetron sputtering has several drawbacks, which has made it very difficult to produce bulk materials. These drawbacks include unwanted target reactions, transport limitations, and low growth rates. During reactive magnetron sputtering, micro-arcs can occur on the cathode surface which cause imperfections in the deposited material. Another problem associated with this process is the “disappearing anode” effect, in which the

entire anode becomes covered by randomly grown insulating layers. Also related to this process is the problematic formation of an insulating nitride layer on the target surface that increases the impedance of the cathode until the target becomes "poisoned" or completely insulating. This results in a drastic decrease in deposition rates to almost zero when the target becomes too nitrided to operate. Materials transport can also be a problem in bulk crystal growth using magnetron sputtering since there can be a significant loss of material to the sidewalls.

The present invention is provided to address these and other problems associated with the growth of thin films and bulk materials.

Disclosure of the Invention

According to one method of the present invention, a single-crystal $M^{III}N$ article is produced. A template material having an epitaxial-initiating growth surface is provided. A Group III metal target is sputtered in a plasma-enhanced environment to produce a Group III metal source vapor. The Group III metal source vapor is combined with a nitrogen-containing gas to produce reactant vapor species comprising the Group III metal and nitrogen. The reactant vapor species is deposited on the growth surface to produce a single-crystal $M^{III}N$ layer thereon. The template material is removed, thereby providing a free-standing, single-crystal $M^{III}N$ article having a diameter of approximately 0.5 inch or greater and a thickness of approximately 50 microns or greater.

Methods of the present invention can be implemented by providing a novel sputter material transport device to enhance thin-film and bulk material manufacturing processes. The novel transport device is capable of ultra-high

deposition and growth rates, making it feasible for growing thick material and increasing throughput in manufacturing processes. The transport device can be used both to grow bulk crystalline materials and to deposit thin films and epitaxial layers onto bulk substrates. Generally, as compared to other sputter processes, the transport device has the advantages of lowered processing pressure, higher deposition rates, higher ionization efficiency, and a controlled processing environment with no contamination. The transport device utilizes an enhanced sputtering process to rapidly deposit both metallic and dielectric materials. This enhancement allows the process to overcome the limitations of conventional PVD techniques.

The transport device according to the present invention can achieve growth rates in excess of ten times those achieved by any other direct deposition process. As currently tested, the device is capable of depositing single or polycrystalline material at a rate in excess of approximately 60 μm/hr. This high deposition rate allows for high throughput capabilities and the possibility of manufacturing bulk materials in short time periods. The device has increased growth rates due to the very high ionization efficiencies, which enhances the sputtering process without "poisoning" the sputtering material. The ability to deposit material at high deposition rates will have many commercial applications, including high-throughput manufacturing processes of thick films of exotic materials. Moreover, high-quality material can be deposited in a cost-effective manner. It is also projected that the device will aid in the commercialization of bulk dielectric and semiconductor materials and will have numerous applications to other materials.

The transport device surpasses present technology by offering a non-contaminating method, in the form of a triode sputtering arrangement, to increase the ionization efficiency and hence the overall deposition rate. The device also has the advantage of a cooler operating temperature than a thermionic hollow cathode configuration, allowing the injector means of the device to be composed of low-temperature materials, and thus can apply to a broad range of materials as compared to conventional processes. The transport device can increase the deposition rate of the target material and lower the sputtering pressure, thereby enabling a line-of-sight deposition process.

The transport device is capable of growing bulk material such as aluminum nitride and other Group III nitrides and also is capable of depositing metal in deep trenches for the semiconductor industry.

According to the present invention, the transport device includes a magnetron source and a non-thermionic electron (or, in effect, a plasma) injector assembly to enhance magnetron plasma. Preferably, the electron/plasma injector is disposed just below the surface of a cathode target material, and includes a plurality of non-thermionic, hollow cathode-type injector devices for injecting electrons into a magnetic field produced by a magnetron source. The injector can be scaled in a variety of configurations (e.g., circular or linear) to accommodate various magnetron shapes. When provided in the form of a circular ring, the injector includes multiple hollow cathodes located around the inner diameter of the ring.

The transport device constitutes an improvement over previously developed hollow cathode enhanced magnetron sputtering devices that rely on thermionic emission. The device of the present invention comprises a non-

thermionic electron emitter that operates as a "cold" plasma source and can be composed of the same material as its sputtering target. The injector can be manufactured out of high-purity metals (e.g., 99.9999%), thereby eliminating a source of contamination in the growing film. The addition of the injector to the magnetron sputtering process allows higher deposition rates as compared to rates previously achieved by conventional magnetron sputtering devices. Moreover, the transport device takes advantage of the hollow cathode effect by injecting electrons and plasma into the magnetic field to increase plasma densities without the contamination problem associated with a traditional, thermionic-emitting tantalum tip. As disclosed above, the transport device is further characterized by a decreased operating pressure and an increased ionization rate over conventional magnetron sputtering.

Therefore, according to another method of the present invention, a single-crystal $M^{III}N$ article is produced by using a sputtering apparatus comprising a non-thermionic electron/plasma injector assembly to produce the Group III metal source vapor from a Group III metal target. The Group III metal source vapor is combined with a nitrogen-containing gas to produce reactant vapor species comprising Group III metal and nitrogen. The reactant vapor species is deposited on the growth surface of the template material to produce a single-crystal $M^{III}N$ layer thereon.

The sputter transport device comprises a sealable or evacuable, pressure controlled chamber defining an interior space, a target cathode disposed in the chamber, and a substrate holder disposed in the chamber and spaced at a distance from the target cathode. The target cathode is preferably bonded to a target cathode holder and negatively biased. A magnetron assembly is disposed

in the chamber proximate to the target cathode. A negatively-biased, non-thermionic electron/plasma injector assembly is disposed between the target cathode and the substrate holder. The injector assembly fluidly communicates with a reactive gas source and includes a plurality of hollow cathode-type structures. Each hollow cathode includes an orifice communicating with the interior space of the chamber.

According to one aspect of the present invention, the electron/plasma injector assembly is adapted for non-thermionically supplying plasma to a reaction chamber. The injector assembly comprises a main body and a plurality of replaceable or interchangeable gas nozzles. The main body has a generally annular orientation with respect to a central axis, and includes a process gas section and a cooling section. The process gas section defines a process gas chamber and the cooling section defines a heat transfer fluid reservoir. The gas nozzles are removably disposed in the main body in a radial orientation with respect to the central axis and in heat transferring relation to the heat transfer fluid reservoir. Each gas nozzle provides fluid communication between the process gas chamber and the exterior of the main body.

The methods of the present invention can be utilized to successfully produce device-quality articles.

According to one embodiment of the present invention, a bulk single-crystal $M^{III}N$ article has a diameter of approximately 0.5 inch to approximately 12 inches and a thickness of approximately 50 microns or greater.

According to another embodiment of the present invention, a single-crystal $M^{III}N$ article is produced in wafer form, having a thickness ranging from approximately 50 microns to approximately 1mm.

According to yet another embodiment of the present invention, a single-crystal $M^{III}N$ article is produced in boule form, having a diameter of approximately 2 inches or greater and a thickness ranging from approximately 1mm to greater than approximately 100mm.

According to still another embodiment of the present invention, the single-crystal $M^{III}N$ layer is used as a seed crystal, such that additional reactant vapor species comprising the Group III metal and nitrogen can be deposited the $M^{III}N$ layer to produce a bulk, homoepitaxially grown $M^{III}N$ article.

In conjunction with the methods of the present invention wherein a bulk $M^{III}N$ article is produced, a wafer can be cut from the $M^{III}N$ article and an epitaxial layer subsequently deposited on the wafer.

The single-crystal $M^{III}N$ layers or articles produced according to the methods of the present invention can be formed at a growth rate greater than approximately 10 microns/hour.

In conjunction with the methods of the present invention, microelectronic or optoelectronic devices or components can be fabricated on the $M^{III}N$ layers or articles, or on any additional layer grown on the $M^{III}N$ layers or articles.

According to a further embodiment of the present invention, a highly-oriented polycrystalline Group III nitride material is provided. The material has an elongate surface and a plurality of grain boundaries oriented substantially normal to the elongate surface. Thermal conductivity is high (i.e., promoted or enhanced) through the thickness of the material in a direction substantially normal to the elongate surface, and is low (i.e., impeded) in a direction substantially parallel to the elongate surface. The material is transparent to radiative energy in the infrared spectrum, the microwave spectrum, or both

spectra, along the direction substantially normal to the elongate surface. As part of the growth process of the material, the material can be bonded to a metallic frame and employed in applications in which its directional thermal conductivity and/or its transparency is advantageous.

According to a further method of the present invention, a window is produced that is adapted to transmit radiative energy in the infrared and/or microwave spectra. A negatively-biased target cathode including a target material is provided in a sealed chamber. A metallic frame is provided in the chamber and spaced at a distance from the target cathode. An operating voltage is applied to the target cathode to produce an electric field within the chamber. A magnetron assembly is provided in the chamber to produce a magnetic field within the chamber. A negatively-biased, non-thermionic electron/plasma injector assembly is provided between the target cathode and the metallic frame to create an intense plasma proximate to the target cathode. A background gas is introduced into the chamber to provide an environment for generating a plasma medium. A portion of the target material is sputtered and transported through the plasma medium toward the metallic frame.

It is therefore an object of the present invention to provide low-defect density, single-crystal Group III nitride articles, substrates and device layers characterized by purities and sizes that previously have been unattainable.

It is another object of the present invention to provide a novel sputter material transport method and device capable of ultra-high deposition and growth rates of low-defect density Group III nitride materials.

It is a further object of the present invention to provide a polycrystalline material in bulk form which can transmit infrared and/or microwave energy.

Some of the objects of the invention having been stated hereinabove, other objects will become evident as the description proceeds when taken in connection with the accompanying drawings as best described hereinbelow.

Brief Description of the Drawings

Figure 1 is a side elevation view of a heterostructure provided in accordance with the present invention;

Figure 2 is a side elevation view of a free-standing, bulk article produced according to the present invention;

Figure 3A is a side elevation view of the bulk article illustrated in Figure 2 with an additional layer deposited thereon;

Figure 3B is a side elevation view of a heterostructure similar to that illustrated in Figure 1 with an additional layer deposited thereon;

Figure 4A is a side elevation view of the bulk article illustrated in Figure 2 with a device fabricated thereon;

Figure 4B is a side elevation view of the heterostructure illustrated in Figure 3A with a device fabricated thereon;

Figure 4C is a side elevation view of the heterostructure illustrated in Figure 1 with a device fabricated thereon;

Figure 4D is a side elevation view of the heterostructure illustrated in Figure 3B with a device fabricated thereon;

Figure 5A a side elevation view of a heterostructure with interlayers deposited thereon in preparation for lateral epitaxial overgrowth;

Figure 5B is a side elevation view of the heterostructure illustrated in Figure 5A after patterning and lateral epitaxial overgrowth procedures have been performed;

Figure 6 is a side elevation view of a window including a highly transparent, highly oriented polycrystalline material produced according to the present invention;

Figure 7 is a schematic view of a novel sputter transport device according to one embodiment of the present invention;

Figure 8A is a top plan view of an electron/plasma injector assembly provided according to one embodiment of the present invention;

Figure 8B is a cut-away vertical cross-sectional view of the injector assembly illustrated in Figure 8A taken along line 8B-8B thereof;

Figure 9 is a schematic view of a novel sputter transport device according to a further embodiment of the present invention;

Figure 10 is a perspective view of an electron/plasma injector assembly according to another embodiment of the present invention;

Figure 11 is a top plan schematic view of the injector assembly illustrated in Figure 10;

Figure 11A is a vertical cross-sectional view of the injector assembly illustrated in Figure 11 taken along line 11A-11A thereof;

Figure 11B is a vertical cross-sectional view of the injector assembly illustrated in Figure 11 taken along line 11B-11B thereof;

Figure 12A is another perspective view of the injector assembly illustrated in Figure 10;

Figure 12B is a top plan view of the injector assembly illustrated in Figure 10;

Figure 13 is a perspective view of the injector assembly illustrated in Figure 10 showing the operation thereof and an exemplary electron/plasma injection pattern;

Figure 14 is a plot comparing the source performance of a transport device provided according to the present invention and that of a conventional magnetron source;

Figure 15 is a perspective view of a rectangular magnetron source which can be employed in combination with the present invention;

Figure 16 is a schematic view of a novel sputter transport device according to an additional embodiment of the present invention; and

Figure 17 is a schematic view of a novel sputter transport device according to a yet another embodiment of the present invention.

Detailed Description of the Invention

For purposes of the present disclosure, it will be understood that when a given component such as a layer, region or substrate is referred to herein as being disposed or formed "on" another component, that given component can be directly on the other component or, alternatively, intervening components (for example, one or more buffer layers, interlayers, electrodes or contacts) can also be present. It will be further understood that the terms "disposed on" and "formed on" are used interchangeably to describe how a given component is positioned or situated in relation to another component. Hence, the terms

"disposed on" and "formed on" are not intended to introduce any limitations relating to particular methods of material transport, deposition, or fabrication.

The terms "$M^{III}N$," "M^{III} nitrides," and "Group III nitrides" are used herein to describe binary, ternary, and quaternary Group III nitride based compounds such as aluminum nitride, gallium nitride, indium nitride, aluminum gallium nitride, indium gallium nitride and aluminum indium gallium nitride, and alloys thereof, with or without added dopants or other intentional impurities, as well as all possible crystalline structures and morphologies, and any derivatives or modified compositions thereof.

Terms relating to crystallographic orientations, such as Miller indices and angles in relation to the plane of a layer of material, are intended herein to cover not only the exact value specified (e.g., (116), 45° and so on) but also any small deviations from such exact value that might be observed.

As used herein, the term "epitaxy" generally refers to the formation of a single-crystal film structure on top of a crystalline substrate. Epitaxy can be broadly classified into two categories, namely homoepitaxy and heteroepitaxy. In the case of homoepitaxy, the film and the underlying substrate have the same structural relationships. Reasons for extending the substrate through the deposition thereon of an epitaxial film layer, or "epilayer," of the same composition include the observations that the epitaxial layer (1) is typically much more free of defects as compared to the substrate, (2) is typically purer than the substrate, and (3) can be doped independently of the substrate. The respective lattice parameters of the epilayer and substrate are perfectly matched, with no interfacial bond straining.

In heteroepitaxy, on the other hand, the film and substrate have different compositions. Moreover, the respective lattice parameters are, by definition and to a varying degree, mismatched in the case of heteroepitaxy. Heteroepitaxy has been accomplished in some processes that result in a quite small lattice mismatch, such that the heterojunction interfacial structure is similar to a homoepitaxial structure. Nevertheless, thermal mismatch (i.e., a difference in the respective thermal expansion coefficients between the film and substrate) as well as distinctions in the respective chemistries of the film and substrate can exist to degrade electronic properties and interface quality. If the lattice parameters are significantly mismatched, relaxed epitaxy or strained epitaxy results. In the case of relaxed epitaxy, misfit dislocation defects form at the interface between the film and the substrate. In the case of strained epitaxy, the respective lattices of the film and the substrate tend to strain in order to accommodate their differing crystallographies.

As used herein, the term “device” is interpreted to have a meaning interchangeable with the term “component.”

Referring now to Figure 1, a heterostructure, generally designated **10**, is illustrated according to the invention. Heterostructure **10** comprises a base substrate **12** on which a single-crystal, low-defect density $M^{III}N$ layer **14** is epitaxially grown. Preferably, base substrate has a diameter of 0.5 inch or greater. Base substrate **12** has a growth surface **12A** having a composition and structure that enables base substrate **12** to serve as a template for the epitaxial growth of $M^{III}N$ layer **14** thereon. Alternatively, a buffer layer or interlayer **16** is grown on base substrate **12** so as to provide a suitable epitaxy-initiating growth surface **16A** for $M^{III}N$ layer **14**.

Non-limiting examples of material compositions suitable for use as base substrate **12** include sapphire, silicon, silicon carbide, diamond, lithium gallate, lithium aluminate, $ScAlMgO_4$, zinc oxide, spinel, magnesium oxide, gallium arsenide, glass, tungsten, molybdenum, hafnium, halfnium nitride, zirconium, zirconium nitride, carbon, silicon-on-insulator, carbonized silicon-on-insulator, carbonized silicon-on-silicon, and gallium nitride. Moreover, the particular base substrate selected could be characterized as being a conductive substrate, an insulating substrate, a semi-insulating substrate, a twist-bonded substrate, a compliant substrate, or a patterned substrate.

Non-limiting examples of material compositions suitable for use as interlayer **16** include gallium nitride, aluminum nitride, indium nitride, zinc oxide, silicon carbide, and their alloys. Interlayer **16** could also be composed of SiO_2, SiN, diamond, lithium gallate, lithium aluminate, zinc oxide, spinel, magnesium oxide, gallium arsenide, tungsten, molybdenum, hafnium, hafnium nitride, zirconium, zirconium nitride, and carbon.

Preferably, base substrate **12** has a thermal coefficient of expansion that is substantially equal to that of $M^{III}N$ layer **14** in order to minimize thermal mismatch. When interlayer **16** is first deposited on growth surface **12A**, however, thermal mismatch as between base substrate **12** and $M^{III}N$ layer **14** is of less concern.

According to one method of the invention, base substrate **12** and a Group III metal target are loaded into a sputter deposition chamber. A highly energetic plasma-enhanced environment is generated in the chamber, using a suitable background gas such as argon. Separate nitrogen-containing source gas is conducted into the chamber. Alternatively, the gas utilized to generate the

plasma could also be used as the reactant source gas, in which case the background gas provides the nitrogen species. The Group III metal target is sputtered to produce a Group III metal source vapor. The Group III metal source vapor combines with the nitrogen-containing gas, which is characterized as including one or more species such as diatomic nitrogen, atomic nitrogen, nitrogen ions, and partially ionized nitrogen, as well as nitrogen-containing compounds such as ammonia. As a result, reactant vapor species comprising components of the Group III metal and the nitrogen are produced within the reaction chamber, and are deposited on growth surface **12A** of base substrate **12** (or on growth surface **16A** when first depositing buffer layer **16**). The as-deposited reactant vapor species grows epitaxially on growth surface **12A** to produce single-crystal $M^{III}N$ layer **14**. $M^{III}N$ layer **14** can be doped by conducting conventional doping methods, such as by introducing dopant-containing gases into the reaction chamber under controlled conditions.

In one aspect of the invention, the growth of $M^{III}N$ layer **14** is permitted to continue until its thickness is sufficient to ensure that the bulk crystal has a defect density low enough to be considered as device-quality. In addition, $M^{III}N$ layer **14** can be rotated as it grows according to conventional methods. The structure is then removed from the reaction chamber, and base substrate **12** is separated or removed from $M^{III}N$ layer **14**. The technique employed to remove base substrate **12** from $M^{III}N$ layer **14** can be, for example, polishing, chemomechanical polishing, laser-induced liftoff, cleaving, wet etching, or dry etching. The choice of the removal technique will depend on the particular composition of base substrate **12**. Similarly, if wet etching is desired, the choice of the etchant will likewise depend on the particular composition of base

substrate **12**. Moreover, if dry etching is desired, the choice of the particular dry etching technique will likewise depend on the particular composition of base substrate **12**.

Referring to Figure 2, upon completion of the substrate removal process, a bulk, free-standing, single-crystal $M^{III}N$ article **20** is produced. In accordance with the invention, article **20** has a diameter **d** of 0.5 inch or greater, a thickness **t** of 50 microns or greater, and a defect density of no greater than 10^9 defects/cm^3. Article **20** can be doped according to known methods. In the production of alloys and compounds, the resulting composition can have greater than 50% Group III metal and nitrogen components.

In order to produce article **20** having the dimensions and properties just described, an important step in the inventive process is the technique by which the components of $M^{III}N$ layer **14** are transported to growth surface **12A** of base substrate **12**. According to the invention, sputtering is performed in favor of other physical vapor deposition techniques, as well as in favor of chemical vapor deposition and other vapor phase techniques. Preferably, the sputtering is accomplished by a novel non-thermionic, plasma-enhanced sputtering technique as described hereinbelow, and at a growth rate greater than 10 microns/hour.

If an interlayer **16** is to be formed on growth surface **12A**, such interlayer **16** can be deposited by any number of techniques, including physical vapor deposition (such as sputtering), molecular beam epitaxy, atmospheric chemical vapor deposition, low pressure chemical vapor deposition, plasma-enhanced chemical vapor deposition, metallorganic chemical vapor deposition, evaporation, sublimation, and hydride vapor phase epitaxy. Base substrate **12**

can then be separated from $M^{III}N$ layer **14** by removing interlayer **16** using a chemical etching, cleaving, laser liftoff, or other suitable removal technique.

Bulk crystal article **20** shown in Figure 2 can be produced in the form of a wafer, in which case the thickness will be in the range of 50 microns to 1 mm. Multiple wafers can be produced either one at a time or by providing more than one base substrate **12** in the reaction chamber. As part of a further fabrication process, a major surface of the wafer can be prepared for epitaxial growth according to known methods, such as polishing, after which an epitaxial layer of suitable composition can be deposited on the prepared surface.

In addition, the method of the invention enables the production of bulk crystal article **20** in the form of a boule, in which case the diameter is at least 2 inches and the thickness is from between 1 mm to greater than 100 mm. Multiple wafers can be cut from the boule using a wafer saw, and subsequently prepared for epitaxy.

Referring to Figure 3A, another heterostructure, generally designated **30**, is illustrated according to the invention. As shown, $M^{III}N$ article **20** can serve as a seed crystal for the homoepitaxial growth of a bulk, second $M^{III}N$ layer **32** characterized by having a defect density even lower than that of $M^{III}N$ article **20**. According to this method, $M^{III}N$ article **20** has a thickness of approximately 50 to 1,000 microns. As similarly described above, article **20** can be removed to produce the free-standing bulk crystal shown for example in Figure 2, which in this embodiment corresponds to $M^{III}N$ layer **32**. According to this method, $M^{III}N$ layer **32** has a thickness of approximately 0.1 to approximately 100 mm and a diameter greater than approximately 0.5 inch. Additionally, $M^{III}N$ layer **32** can be

grown in wafer or boule form as described hereinabove. Wafers can be sliced from the boule as described hereinabove.

$M^{III}N$ layer **32** can be deposited on growth surface **20A** of article **20** by any number of techniques, including physical vapor deposition (e.g., sputtering), molecular beam epitaxy, atmospheric chemical vapor deposition, low pressure chemical vapor deposition, plasma-enhanced chemical vapor deposition, metallorganic chemical vapor deposition, evaporation, sublimation, and hydride vapor phase epitaxy.

Referring to Figure 3B, another heterostructure, generally designated **35,** is illustrated according to the invention. As shown, $M^{III}N$ layer **14** can serve as a seed crystal for the homoepitaxial growth of a bulk, second $M^{III}N$ layer **36** characterized by having a defect density even lower than that of first $M^{III}N$ layer **14.** According to this method, first $M^{III}N$ layer **14** is grown as a thin film with a thickness of approximately 10 to 10,000 nm. As described above, base substrate **12** can be removed to produce free-standing bulk crystal **20** shown in Figure 2, which in this embodiment corresponds to $M^{III}N$ layer **36**. Additionally, $M^{III}N$ layer **36** can be grown in wafer or boule form as described hereinabove. Wafers can be sliced from the boule as described hereinabove.

Second $M^{III}N$ layer **36** can be deposited on growth surface **14A** by any number of techniques, including physical vapor deposition, (e.g., sputtering), molecular beam epitaxy, atmospheric chemical vapor deposition, low pressure chemical vapor deposition, plasma-enhanced chemical vapor deposition, metallorganic chemical vapor deposition, evaporation, sublimation, and hydride vapor phase epitaxy.

Referring now to Figures 4A – 4D, $M^{III}N$ article **20** and layers **14**, **32**, and **36** produced according to the invention are device-quality materials that can serve as platforms for the fabrication of one or more microelectronic devices, optoelectronic devices, and/or other electronic components **38**. Non-limiting examples of devices **38** include light-emitting diodes, detectors, biological or chemical sensors, filters, transistors, rectification circuitry, semiconductor lasers., bond pads, metallization elements, and interconnects.

Referring to Figure 5A, another heterostructure, generally designated **40**, is illustrated according to the invention in which a lateral epitaxial overgrowth method is implemented. In this embodiment, interlayer **16** and/or an additional interlayer **18** (which can have a composition different from that of interlayer **16**) is deposited on base substrate **12**, and is then patterned using a conventional masking and/or etching technique to form a patterned (for example, striped) layer **42**. Using the enhanced sputtering technique described herein, a reactant vapor species comprising Group III metal and nitrogen components is then transported toward patterned layer **42** and exposed portions **42A** of layer **42**. A device-quality, bulk single-crystal $M^{III}N$ layer **44** begins to grow upwardly from exposed portions **42A** of layer **42**, and then grows laterally over the tops of patterned layer **42**. Upon continued growth of $M^{III}N$ layer **44**, the growing crystal coalesces to form a continuous, low-defect density layer.

Referring now to Figure 6, the non-thermionic, plasma-enhanced sputtering technique described hereinbelow can be utilized to produce an infrared and/or microwave-transparent, bulk-form, Group III nitride window, generally designated **50**, which is characterized by a high purity and a highly oriented polycrystalline morphology. Window **50** generally includes a bulk Group

III nitride (such as aluminum nitride or gallium nitride) window material **52** supported in a metallic frame **54**. Window material **52** has properties approaching theoretical bulk values, including a thermal conductivity of 320 W/m*K in the case of aluminum nitride. Because of its high thermal conductivity, window material **52** is resistant to thermal shock. Moreover, a thickness of greater than approximately 50 μm is possible. The transparency of window material **52** is greater than approximately 65%.

As illustrated in Figure 6, window material **52** includes an outer elongate surface **52A** and an inner elongate surface **52B**. A plurality of grain boundaries **52C** are oriented substantially normal to elongate surfaces **52A** and **52B**. Thus, window material **52** will readily conduct heat energy **H** through its thickness in the direction generally normal to elongate surfaces **52A** and **52B** (that is, generally along grain boundaries **52C**). Heat energy **H** is impeded, however, in directions generally parallel to elongate surfaces **52A** and **52B**. In use, heat energy **H** can be carried away from inner elongate surface **52B** by supplying a heat transfer medium **G**, such as hydrogen or helium, proximate or adjacent to inner elongate surface **52B**. An advantage of the production of window **50** according to methods of the present invention is that window material **52** can be directly bonded to a metallic frame **54** as an inherent step of the growth process. Metallic frame **54** can be provided in a number of different shapes and cross-sectional profiles, and can be employed as a structural support for window material **52** in a subsequent installation procedure. An initial substrate may be provided on which window material **52** grows, and thereafter removed by etching or other known removal processes.

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Window **50** has several useful applications, including microwave windows for high-power radars, infrared windows for high-speed heat-seeking missiles, windows for optical monitors in high-temperature manufacturing processes, windows for optical sensors in turbine engines and in power plants, materials for electronic substrates, and heat-spreading components in high-power electronic devices. Bulk-form aluminum nitride or gallium nitride available from other sources (such as by sintering and other ceramic powder processing techniques) does not meet the requirements for IR and microwave-transparent windows, largely due to the contaminates present in the bulk as a result of conventional manufacturing techniques. For example, ceramic powder processing techniques require oxide binders which clog the grain boundaries and consequently reduce infrared and microwave transmission.

In the embodiments of the invention described hereinabove, at least one $M^{III}N$ layer is epitaxially grown by a high-growth rate sputtering technique. The sputtering process is accomplished by either conventional techniques or, in a preferred process, by implementing a novel enhanced sputtering technique described hereinbelow.

A conventional sputtering technique utilizes a parallel-plate, planar diode configuration in which a cathode and an anode spaced apart from each other in a sealable reaction chamber by an electrode gap. The cathode is driven negative by a power supply. A glow-discharge plasma is generated between the two electrodes and confined by a grounded metal vacuum containment wall of the reaction chamber. To "strike" (initiate) the discharge, it is often necessary to supply a spike of higher voltage, or to adjust pressure to a minimum so that the gas will break down at the voltage available. The voltage drop across the sheath

of the plasma results in high-energy ion bombardment of the cathode by positive ions and sputtering of the cathode. The cathode voltage drop also sustains the plasma by accelerating secondary electrons emitted from the cathode into the plasma where they initiate a cascade of ionizing collisions. The diode can be operated under an applied DC voltage or an RF voltage. RF excitation is required when sputtering insulating targets.

A mode of plasma-enhanced chemical activation generally known as "reactive sputtering" uses a sputtered source material along with a gaseous one. The gas becomes dissociated in the sputtering plasma and reacts to form a compound film. The parallel-plate plasma configuration can be used to supply vapor for film deposition by sputter-erosion of the cathode, which serves as the target material. Often, the plasma is magnetized using a magnetron assembly. A reactive gas (e.g., N_2) is added to the sputtering plasma (e.g., argon gas plasma) in order to shift compound-film stoichiometry in sputtering from a compound target, or to deposit a compound film from a metallic target (e.g., Al). Compound deposition by reactive sputtering from a metallic target generally lowers target fabrication costs and increases target purity as compared to using a compound target, although process control can be more difficult if film composition is critical.

When employing a planar-diode plasma configuration to cause sputtering, the beam electrons ejected from the cathode must undergo enough ionizing collisions with the gas to sustain plasma before the beam electrons reach the anode and are removed there. This requirement places a lower limit on operating pressure, and can be enhanced through the use of a magnetron assembly. The magnetron assembly typically includes a central bar magnet and

an outer ring magnet or magnets of opposite pole. The magnetron produces a cross-wise magnetic field over the cathode. The magnetic field traps the beam electrons in orbits near the cathode surface. As a result, the path lengths of the beam electrons are significantly increased before the electrons finally escape to the anode by collisional scattering. Because the paths of the electrons become longer than the electrode gap, the minimum pressure needed to sustain the plasma is much lower (typically 0.1 Pa rather than 3 Pa) when using a magnetron as compared with a planar diode without a magnetron. At a lower pressure (e.g., 0.1 Pa), the sputtered particles retain most of their kinetic energy upon reaching the substrate, and this energy has advantageous effects on the structure of the depositing film. In addition, deposition rate is increased due to reduced scattering and redeposition of sputtered particles on the cathode. Moreover, the beam electrons are utilized more efficiently, with the result that a lower applied voltage (e.g., approximately 500 V) is required to sustain a plasma of a given density, and the voltage increases less steeply with power input as compared to a non-magnetron planar diode configuration.

A typical magnetron has a planar, circular configuration. The target material of the cathode is a disc, typically 3 - 10 mm thick, and is bonded (such as by soldering, for good thermal contact) to a water-cooled copper backing plate. The water coolant can be deionized to prevent electrolytic corrosion between the electrically-biased backing plate and a grounded water supply. The cathode is often floated off ground with a ceramic insulating ring. The containment wall of the reaction chamber serves as an anode, although grounded shields can be added to confine the sputtered material. The cross-wise magnetic field is established by the magnets. The magnets are connected

on the back by an iron "field-return" plate to complete the magnetic circuit and to confine the magnetic field.

Upon igniting plasma, beam electrons emitted from the cathode are accelerated into plasma by the electric field of the cathode sheath. The presence of the magnetic field causes the beam electrons to curve into orbits as a result of the Lorentz force, $F = F_E + F_B = q_eE + q_ev \times B$. The radius of the orbit (referred to as the gyratron, cyclotron or Larmor radius) depends on the strength of the magnetic field and on the electron velocity component perpendicular to the magnetic field. In order for the magnetic field to have an effect on the beam electrons, the pressure must be low enough (typically less than a few Pa) that the electron mean free path is not significantly less than the orbit radius. If this condition is met, the beam electrons are said to be "magnetized" although the ions are not magnetized. The magnetron can operate as a sputtering source at much higher pressures, but in such cases gas scattering dominates the behavior of the beam electrons instead of the magnetic field itself.

Under lower pressure conditions, the beam electrons emitted from the target surface of the cathode or created by ionization in the sheath field are accelerated vertically by the electric field and simultaneously forced sideways by the magnetic field. The beam electrons eventually reverse direction and return toward the target. As the beam electrons are thus directed toward the target, they decelerate in the electric field until their direction is again reversed, and the cycle repeats. The net motion or path of these electrons is a circular drift path around the circle of the target. This drift path is in the direction of the **E x B** vector product. The magnetron is ordinarily designed such that the **E x B** drift

path closes on itself so that the beam electrons do not pile up or accumulate at some location.

Preferably, the plasma generated in the reaction chamber is enhanced by taking advantage of the "hollow cathode" effect, a phenomenon which generally involves utilizing geometric means to trap secondary electrons emitted from an ion-bombarded target cathode. When a hollow-cathode-type structure is driven to a very high discharge current, its cathode surfaces heat to a temperature sufficient to cause thermionic emission of electrons, and the local plasma glow discharge will enter the arc mode. A hollow cathode, typically constructed of a refractory material and provided with a local gas supply, can be a useful source of moderately energetic electrons for plasmas. The hollow cathode is provided in the form of a tube having a tantalum tip. A gas source is connected to one end of the hollow cathode, and a small aperture or orifice is provided at the tip. The aperture restricts the gas flow and results in a large pressure differential across tip. The inner pressure of the hollow cathode is typically in the range of several hundred mTorr. Electrons are emitted by biasing the hollow cathode negatively with respect to the local plasma potential (which is usually the ground potential). A hollow cathode having a diameter of only a few millimeters can be employed to produce an electron current of several to ten amperes. An external heater or a short-term, high-voltage spike is typically used to heat the hollow cathode to the temperature required for emission.

The hollow cathode is situated in the fringe region of the magnetic field of the magnetron to supply additional electrons to the magnetron discharge. The hollow cathode serves to decouple the current-voltage relation of the diode plasma and allow operation of the plasma at wide ranges of voltage and current,

as well as to lower the operating pressure in chamber. The hollow cathode can operate at 0.1 mTorr, which is below the range of the more conventional magnetron/diode arrangement described hereinabove. If conventional magnetron/diode arrangements were to operate at these lower pressures, there would be not be enough gas atoms for efficient ionization by the secondary electrons. The additional supply of electrons from the hollow cathode, however, removes this limitation and allows operation at approximately 0.1 mTorr for magnetron arrangements, and approximately 0.5 mTorr for RF-diode arrangements. Such pressures are well into the long mean free path mode, and sputtered atoms or ions move in straight, line-of-sight trajectories without gas scattering.

While hollow cathode enhanced sputtering devices provide advantages over other sputter deposition techniques, there are still drawbacks with regard to their use, owing to the fact that they are thermionic emitting electron devices. For instance, contamination is still observed to be a problem, particularly since the hollow cathode tip material tends to evaporate and mix with the growing deposition material. Another problem relates to the intense heat produced by thermionic emission, which can damage the growing material. Therefore, in accordance with a preferred embodiment of the present invention, a novel sputter transport device is provided that is characterized by the use of a non-thermionic electron/plasma injector assembly.

Referring now to Figure 7, a non-thermionic sputter transport device, generally designated **100**, is illustrated. Key operating components of transport device **100** are contained within a grounded, sealable sputter-transport chamber **102**. As will be appreciated by persons skilled in the art, a pumping system (not

shown) is provided to control the pressure (vacuum or otherwise) within chamber **102**. Supply systems (not shown) are also provided for delivering a background gas (e.g., argon), and a reactive gas (e.g., nitrogen) in the case of reactive sputtering, into chamber **102**. In some applications of the present invention, the reactive gas may also serve as the background gas.

A cathode **104** constructed from a metallic, dielectric, or compound target material is bonded to a target holder **106** to establish thermal contact therebetween. Target cathode **104** may be provided in the form of a circular disk or a rectilinear plate, or may have some other shape. Target holder **106** is preferably constructed of copper or other relatively inexpensive material that offers acceptable levels of both thermal and electrical conductivity. A heat exchanger system (not shown) is provided to circulate a heat transfer medium such as water through target holder **106** to keep target holder **106** (and thus target cathode **104**) cool. A magnetron assembly **110** includes a set of oppositely-poled magnets **112** and **116** connected by a magnetic field return plate **118**. The arrangement of magnets **112** and **116** preferably constitutes a central magnetic bar **112** surrounded by an outer magnetic annulus **116**, although other arrangements and shapes could be provided. Magnets **112** and **116** are preferably located on the side of target holder 106 opposite to target cathode **104**. A negative bias voltage is applied to target holder **106** by connecting target holder **106** in series with a voltage source **120**.

A substrate holder **130**, which serves as the primary anode, is disposed in chamber **102** in parallel with and spaced at a distance from target cathode **104**. Preferably the spacing is in the range of approximately 2 cm to 20 cm. Substrate holder **130** can be constructed from any material that is either electrically

conductive or isolated, and can be provided as either a cooling structure or a heating structure. It is preferable that transport device **100** be oriented such that target cathode **104** is physically situated opposite to substrate holder **130**, but can be either vertically above or below substrate holder **130**. A substrate **132** is disposed on substrate holder **130**. Depending on the specific application of transport device **100**, substrate **132** can be either initially provided in bulk form on which a thin-film is to be deposited, or it represents the growing bulk material grown through use of transport device **100**.

As will be appreciated by persons skilled in the art, substrate holder **130** or an associated transfer arm (not shown) can be used to transport substrate holder **130** and, if applicable, an initially-provided substrate material into and out from chamber **102**. In addition, a load lock or similar component (not shown) can be provided to serve as an interface between chamber **102** and the ambient environment to assist in maintaining reduced pressure in chamber **102** when substrate holder **130** and/or an initially-provided substrate material is loaded and thereafter removed from chamber **102**. Other known processing components can used as appropriate to assist in implementing the methods of the invention involving the use of transport device **100**, including an electronic control system, a power supply system, a pressure monitoring system, a mass flow control system, a temperature monitoring system, and a system for automated tracking and transport of workpieces.

As one key aspect of the present invention, an injector assembly generally designated **150** is disposed in chamber **102** proximate to target cathode **104**, and is separately, negatively biased through its serial connection with a voltage source **152**. Hence, injector assembly **150** serves as a cathode apart from and

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additional to target cathode **104**, such that transport device **100** can be characterized as being a triode sputtering source.

Referring to Figures 8A and 8B, injector assembly **150** includes a plurality of injectors **152** serving essentially as individual hollow cathodes. Each injector **152** terminates in an inlet orifice **152A** communicating with the interior of chamber **102** in the region proximate to the surface of target cathode **104**. In the present embodiment, injector assembly **150** takes the form of an injector ring such that each inlet orifice **152A** faces radially inwardly with respect to chamber **102**, although individual injectors **152** can be arranged in a linear or other suitable configuration.

In operation, electrons in the form of supplemental or auxiliary plasma beams are non-thermionically emitted from injectors **152** as a result of the increase in electric field strength at these points, such that the electrons are subsequently injected and coupled into the gradient of the magnetic field (represented by virtual field lines **B**) established by magnetron source **110** to generate an intense plasma. Injector assembly **150** may thus be characterized as a cool, non-thermionic electron/plasma source which injects an approximately equal number of ions and electrons into the region illustrated in Figure 7 proximate to target cathode **104**, thereby creating a higher probability of ionization of the target material. An increase in magnetron current is observed due to the added electrons from injector assembly **150**. This effect can be seen as a significant increase in the plasma brightness, as well as a significant increase in the sputter deposition rate. The intense plasma created in the proximity of the surface of target cathode **104** results in the significant increase in deposition rate by more than ten times over conventional techniques. Injector

assembly **150** also serves to electrostatically confine the plasma to form a broad plasma beam **160** directed toward substrate **132**. Due to the bulk mass and/or cooling design of injector assembly **150**, its temperature remains low and accordingly no thermionic emission, evaporation or contamination takes place during deposition.

Transport device **100** can be operated in either continuous DC, pulsed DC, AC or RF mode, which enables transport device **100** to reactively sputter a wide range of both conductive and insulating materials at very high rates. Due to the high percentage of gas ionization, the material of target cathode **104** is sputtered at ultra-high rates sufficient to prevent a detrimental insulating layer from forming on the target surface. In addition, due to the very high ion energies associated with the process according to the present invention, large amounts of material can be sputtered. Device **100** has been proven to operate successfully in 100% reactive gas environments, therefore demonstrating the stability of the device under very reactive conditions.

As described above, a negative bias is applied to target holder **106**, which generates a magnetron sputtering discharge, and a separate negative bias is applied to injector assembly **150**. This generates a very intense plasma, with beamlets of plasma emitting from each injector **152** of injector assembly **150**. The added plasma density and ionization percentage in the region of the target cathode **104** increase the amount of target bombardment, thereby causing increased sputter rates. Due to the increased utilization of sputtering gas, the background processing pressure can be lowered from, for example, approximately 5 mTorr to approximately 0.1 mTorr, which can improve the microstructural properties of materials being formed. This pressure decrease

increases the mean free path of molecules, enabling the creation of plasma beam **160** between target cathode **104** and substrate holder **130** (i.e., the anode) which is characterized by very high ionization efficiency and achievement of ultra-high sputter transport rates.

Referring to Figure 9, a sputter transport device, generally designated **200**, is illustrated according to another embodiment of the present invention. In this particular embodiment, a biased containment shield **202**, constructed from aluminum or other conductive material, is disposed in chamber **102** between target cathode **104** and substrate holder **130** and is surrounded by a containment magnet or magnets **204**. A high voltage applied to containment shield **202** from a voltage source **206** acts to focus the sputtered material and plasma beam **160** onto the growing substrate **132**, thereby increasing the transport efficiency of the sputtered material (such as aluminum nitride) to substrate **132**. Ions and electrons become trapped within the containment region under the influence of the electric and magnetic fields and subsequently deposit on substrate **132**.

Under some circumstances, the user of transport device **100** or **200** might find that the heating of injector assembly **150** causes low-melting-point metals to melt. This problem can be overcome by cooling injector assembly **150** with a copper cooling ring **220**, which is also illustrated in Figure 9.

Referring to Figures 10-13, a preferred embodiment of a fluid-cooled, ring-shaped injector assembly generally designated **300** is illustrated. Injector assembly **300** includes a main body **302** and an outer collar **304** removably secured by clamping screws **306**. Main body **302** includes a process gas section **302A** and a cooling section **302B**. As best shown in Figures 11A and 11B,

process gas section **302A** and outer collar **304** together define a process gas chamber **308**. Individual injectors for supplying electrons and cool plasma, indicated by the reference numeral **310**, are defined by interchangeable gas nozzles **312** fluidly communicating with process gas chamber **308** at one end and with sputter-transport chamber **102** at the other end. Gas nozzles **312** may or may not be constructed from the same material as target cathode **104** and/or containment shield **202**. Cooling section **302B** of main body **302** defines a cooling reservoir **314** adapted to circulate a heat transfer fluid such as water in close proximity to each gas nozzle **312**. The heat transfer fluid is circulated through cooling reservoir **314** by means of a heat transfer fluid inlet conduit **316** and outlet conduit **318**. Process gas such as diatomic nitrogen or argon is supplied to injector assembly **300** by means of a process gas conduit system **320** that communicates with one or more process gas inlets **322** on main body **302**. Figure 13 illustrates one example of an emission pattern of plasma/electrons **310** obtainable by injector assembly **300**. The pattern as well as the gas nozzle pressure can be altered by blocking one or more of individual gas nozzles **312**.

Traditionally, sputter-deposited films have been plagued with low reactive sputter rates, excessive stress, and poor crystalline growth. Due to the non-contaminating nature of transport device **100** or **200**, however, the hollow cathode effect can be advantageously utilized to produce both single-crystal and highly-oriented polycrystalline, bulk-form substrates, such as those described hereinabove, at lower pressures, ultra-high deposition rates, and with minimal material stress. Transport device **100** or **200** is also capable of growing epitaxial layers on substrates. Examples of deposited materials include binary, tertiary,

and quaternary Group III nitride based compounds such as aluminum nitride, gallium nitride, indium nitride, aluminum gallium nitride, indium gallium nitride and aluminum indium gallium nitride, and alloys thereof. Suitable dopants can be added during the growth process. Both single-crystal and polycrystalline morphologies are obtainable. In one specific example, transport device **100** or **200** is capable of growing aluminum nitride purer than that made by powder processing methods and faster than CVD methods. Moreover, because transport device **100** or **200** exhibits a very high degree of sputter particle ionization, transport device **100** or **200** produces a plasma beam environment that facilitates the synthesis of nitride based materials. The material grown by transport device **100** or **200** exhibits the bulk properties of nitrides due to the resulting high crystallinity and purity. In particular, bulk aluminum nitride produced from transport device **100** or **200** has a high IR and UV transmittance, a high thermal conductivity, and a high degree of c-axis orientation.

In addition to growing the materials described hereinabove, transport device **100** or **200** can be utilized to grow a variety of ceramic thin films such as aluminum oxide and zinc oxide, or to deposit copper or other metallic interconnects onto patterned electronic devices. The high transport rate also enables the high-throughput coating of objects.

Figure 14 demonstrates the dramatic improvement in deposition rate by plotting plasma current as a function of applied source voltage with transport device **100** operating under a 0.7A electron enhancement (i.e., with the inventive injector ring installed and supplying current from hollow cathode-type structures), as compared to a typical magnetron sputtering device without any electron enhancement.

Conventional planar magnetron designs suffer from poor target-material utilization because of a trenched erosion pattern that tends to form on the surface of the target material in the vicinity of the **E x B** drift path of the beam electrons. The radial narrowness of this trench results from radial compression of the plasma, which is in turn caused by the well-known "magnetic-mirror" effect. The electrons of the plasma are forced away from both small and large magnetron radii at the sites where the magnetic field converges toward the magnetic pole pieces. The electrons are compressed by these mirrors toward an intermediate radius where the magnetic field is uniform. Both the plasma and the ion bombardment are most intense in the region of magnetic field uniformity. The magnetic-mirror effect can be reduced somewhat by designing a flatter magnetic field or by mechanically scanning the magnets back and forth during sputtering. The non-uniformity of film thickness resulting from plasma compression can be avoided by moving the substrates around during deposition. One simpler, geometric approach to improving uniformity is illustrated in Figure 15, wherein a rectangular magnetron generally designated **410** is utilized. With the rectangular geometry, the many of magnetic field lines B are situated along linear directions, and the beam electrons follow an oblong or "racetrack" **E x B** drift path at target cathode **104**. The rectangular magnetron shape can be employed in connection with the present invention if non-uniformity becomes problematic.

Localization of the plasma over target cathode **104** by the transverse magnetic field of magnetron assembly **110** results in a much lower plasma density over the substrate **132** than in the case of the non-magnetron planar diode, and ion bombardment flux to substrate **132** is reduced accordingly. This

is desirable when the neutral sputtered particles alone carry sufficient kinetic energy to optimize film structure, or when it is important that the substrate heating that results from ion bombardment be kept to a minimum. In other cases, however, it might be desirable to further increase film bombardment while retaining the low operating pressure of the transport device **100** or **200**. One method for increasing ion bombardment of the growing film is to "unbalance" the magnets of magnetron assembly **110**, such as by downsizing central magnet **112** such that the central magnet **112** cannot pull in all the field lines emanating from outer magnets **116**. Hence, in the unbalanced configuration, the magnetic field lines that are not pulled into central magnet **112** will curve away toward substrate holder **130**. Because electrons traveling parallel to a magnetic field are not influenced by the magnetic field, they can escape along these wayward field lines and travel toward substrate **132**. The escaping electrons pull positive ions along with them by ambipolar diffusion and hence increase ion-bombardment flux to substrate **132**. In addition, the bombardment energy can be increased by negatively biasing substrate **132**.

Another way to increase ion-bombardment flux to the growing film is to provide an RF-powered coil to ionize the mostly neutral sputtered-particle flux during transport to substrate **132**. The coil operates by coupling energy inductively into a secondary plasma downstream of the magnetron plasma.

Referring now to Figure 16, a sputter transport device, generally designated **600**, is illustrated according to an additional embodiment of the present invention. Many of the components of sputter transport device are similar to those of sputter transport device **100** shown in Figure 7. In particular injector assembly **150** as described above is utilized to enhance the material

transport process. A primary difference is that a liquid target **604** such as liquid-phase aluminum or gallium is provided as a source species. The target holder in this embodiment is provided in the form of a cup **606** to contain the liquid target material. Preferably, this target holder should be constructed from a material suitable for withstanding the heat involved and which will not contaminate the target material. Candidate materials for target holder **606** include molybdenum and stainless steel. In one embodiment, a 6" diameter molybdenum liquid gallium or aluminum target holder **606** is employed to prevent reaction of the holder with a high purity (99.9999%) liquid gallium or aluminum source **604**. In order to obtain a flat uniform liquid surface of the gallium or aluminum, sufficient wetting of the gallium or aluminum to the molybdenum holder **606** must occur. To this end, grooves can be cut into the bottom of target holder **606** to increase its surface area and thereby increase its wettability. In addition, a breathing hole connecting the grooves can be provided to eliminate any gas trapped under the liquid gallium or aluminum.

Referring now to Figure 17, a sputter transport device, generally designated **700**, is illustrated according to another embodiment of the present invention. Sputter transport device **700** is equipped with a biased containment shield **202** and containment magnets **204**, similar to those described in reference to Figure 9. A high voltage applied to containment shield **202** will focus the sputtered material onto growing substrate or film **132**, thereby increasing the transport efficiency of Ga or Al to substrate or film **132**.

Sputter transport devices **600** and **700** operate as described above. Gallium (or aluminum) particles sputtered from the cathode react with atomic nitrogen in the cathode magnetic fields. The gallium nitride (or aluminum nitride)

particles travel through the containment magnetic field to the substrate. The quality of growth material is determined by the nucleation and growth at the substrate surface.

EXAMPLE 1

An example of a method for manufacturing a GaN single crystal layer on a sapphire substrate by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded on a water-cooled magnetron assembly disposed in a vacuum chamber. The nitrogen-containing gas used to provide the nitrogen source vapor is introduced into the vacuum chamber using mass flow controllers.

A sapphire wafer is cleaned and placed in a wafer platter. The wafer platter is loaded into the vacuum chamber and placed in contact with a substrate heater assembly. The vacuum chamber is then pumped down to 10^{-2} Torr with a mechanical vacuum pump. A diffusion pump is used to reduce the chamber pressure to 10^{-7} Torr. The sample is then heated to a temperature of 1000 °C in 1 hour. The chamber is baked out to a pressure of 10^{-6} Torr. Nitrogen and argon gas are then introduced into the vacuum chamber. The total chamber pressure is 10 mTorr, with an argon partial pressure of 2.5 mTorr and a nitrogen partial pressure of 7.5 mTorr. The plasma is ignited and set to a power of 5kW. The system is held in this configuration for 12 hours. The plasma is then turned off and the heater is ramped to 25 °C in 5 hours. During these stages, a single-crystal GaN layer is formed on the sapphire wafer as represented by, for example, layer **14** in Figure 1 (but disregarding the illustrated buffer layer **16**).

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The gas flow is stopped after the crystal has cooled to room temperature. The GaN crystal is then removed from the chamber. The resulting GaN layer on the sapphire is 300 μm thick and 2 inches in diameter.

The GaN layer can then be released from the sapphire template and prepared for use as a substrate. The sapphire template is removed from the GaN layer using a known removal technique such as, for example, by using a mechanical lapping machine. The resulting GaN wafer has a thickness of approximately 200 μm and a diameter of approximately 2 inches as represented by, for example, article **20** in Figure 2. The GaN wafer is then chemically or mechanically polished by known techniques. The polishing step is followed by a dry etching procedure to produce a surface on the GaN wafer receptive to a thin film of GaN. An epitaxial layer of GaN is then deposited on the prepared surface of the GaN wafer to a typical thickness of approximately 1 to 2 microns by an appropriate process such as, for example, sputtering, MBE, MOCVD, or HVPE. Various devices, components, and/or additional layers can then be formed on the prepared GaN substrate.

EXAMPLE 2

An example of a method for manufacturing a GaN single crystal homoepitaxial layer on a GaN buffer layer on sapphire by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded on a water-cooled magnetron assembly disposed in a vacuum chamber. The nitrogen-containing gas used to provide the nitrogen source vapor is introduced into the vacuum chamber using mass flow controllers.

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A sapphire wafer is cleaned and placed in a wafer platter. The wafer platter is loaded into the vacuum chamber and placed in contact with a substrate heater assembly. The vacuum chamber is then pumped down to 10^{-2} Torr with a mechanical vacuum pump. A diffusion pump is used to reduce the chamber pressure to 10^{-7} Torr. The sample is then heated to a temperature of 1000 °C in 1 hour. The chamber is baked out to a pressure of 10^{-6} Torr. The temperature is then reduced to 500 °C in 10 minutes. Nitrogen and argon gas are then introduced into the vacuum chamber. The total chamber pressure is 10 mTorr, with an argon partial pressure of 2.5 mTorr and a nitrogen partial pressure of 7.5 mTorr. The plasma is turned on at 500W for 1 minute. At this point, a GaN buffer layer is formed on the sapphire wafer as represented by, for example, intermediate layer **16** in Figure 1. The temperature is then increased to 1000 °C in 5 minutes and held for 10 minutes. The plasma is ignited again and set to a power of 5kW. The system is held in this configuration for 12 hours. The plasma is then turned off and the heater is ramped to 25 °C in 5 hours. During these stages, a single-crystal GaN layer is formed on the buffer layer as represented by, for example, layer **14** in Figure 1. The gas flow is stopped after the crystal has cooled to room temperature. The GaN crystal is then removed from the chamber. The resulting GaN layer on the sapphire and buffer layer is 300 μm thick and 2 inches in diameter.

The GaN layer can then be released from the sapphire template and prepared for use as a substrate. The sapphire template is removed from the GaN layer using a known technique such as, for example, by using a mechanical lapping machine. The resulting GaN wafer has a thickness of approximately 200 μm and a diameter of approximately 2 inches as represented by, for example,

article **20** in Figure 2. The GaN wafer is then chemically or mechanically polished by known techniques. The polishing step is followed by a dry etching procedure to produce a surface on the GaN wafer receptive to a thin film of GaN. An epitaxial layer of GaN is then deposited on the prepared surface of the GaN wafer to a typical thickness of approximately 1 to 2 microns by an appropriate process such as, for example, sputtering, MBE, MOCVD, of HVPE. Various devices, components, and/or additional layers can then be formed on the prepared GaN substrate.

EXAMPLE 3

Another example of a method for manufacturing a GaN single crystal layer on a sapphire substrate by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded on a water-cooled magnetron assembly disposed in a vacuum chamber. The nitrogen-containing gas used to provide the nitrogen source vapor is introduced into the vacuum chamber using mass flow controllers.

A sapphire wafer is cleaned and placed in a wafer platter. The wafer platter is loaded into the vacuum chamber and placed in contact with a substrate heater assembly. The vacuum chamber is then pumped down to 10^{-2} Torr with a mechanical vacuum pump. A diffusion pump is used to reduce the chamber pressure to 10^{-7} Torr. The sample is then heated to a temperature of 1000 °C in 1 hour. The chamber is baked out to a pressure of 10^{-6} Torr. Argon gas is introduced into the vacuum chamber through the non-thermionic electron/plasma injector assembly described hereinabove. Nitrogen gas is introduced into the

vacuum chamber near the sapphire wafer substrate. The total chamber pressure is 10 mTorr, with an argon partial pressure of 2.5 mTorr and a nitrogen partial pressure of 7.5 mTorr. The magnetron plasma is ignited and set to a power of 5kW. The plasma supplied by the injector assembly is ignited and set to a power of 1kW. The system is held in this configuration for 3 hours. The plasma is then turned off and the heater is ramped to 25 °C in 5 hours. During these stages, a single-crystal GaN layer is formed on the sapphire wafer as represented by, for example, layer **14** in Figure 1 (but disregarding the illustrated buffer layer **16**). The gas flow is stopped after the crystal has cooled to room temperature. The GaN crystal is then removed from the chamber. The GaN layer on the sapphire is 300 μm thick and 2 inches in diameter.

The GaN layer can then be released from the sapphire template and prepared for use as a substrate. The sapphire template is removed from the GaN layer using a known technique such as, for example, by using a mechanical lapping machine. The resulting GaN wafer has a thickness of approximately 200 μm and a diameter of approximately 2 inches as represented by, for example, article **20** in Figure 2. The GaN wafer is then chemically or mechanically polished by known techniques. The polishing step is followed by a dry etching procedure to produce a surface on the GaN wafer receptive to a thin film of GaN. An epitaxial layer of GaN is then deposited on the prepared surface of the GaN wafer to a thickness of approximately 1 to 2 microns by an appropriate process such as, for example, sputtering, MBE, MOCVD or HVPE. Various devices, components, and/or additional layers can then be formed on the prepared GaN substrate.

EXAMPLE 4

An example of a method for manufacturing a GaN single crystal in boule form on a sapphire substrate by enhanced sputtering of gallium in a nitrogen environment will now be described. Raw materials employed in this method include 99.9999% pure gallium and nitrogen-containing gases such as nitrogen or ammonia. The gallium target used to provide the gallium source vapor is loaded on a water-cooled magnetron assembly disposed in a vacuum chamber. The nitrogen-containing gas used to provide the nitrogen source vapor is introduced into the vacuum chamber using mass flow controllers.

A sapphire wafer is cleaned and placed in a wafer platter. The wafer platter is loaded into the vacuum chamber and placed in contact with a substrate heater assembly. The vacuum chamber is then pumped down to 10^{-2} Torr with a mechanical vacuum pump. A diffusion pump is used to reduce the chamber pressure to 10^{-7} Torr. The sample is then heated to a temperature of 1000 °C in 1 hour. The chamber is baked out to a pressure of 10^{-6} Torr. The temperature is then reduced to 500 °C in 10 minutes. Argon gas is introduced into the vacuum chamber through the non-thermionic electron/plasma injector assembly described hereinabove. Nitrogen gas is introduced into the vacuum chamber near the sapphire wafer substrate. The total chamber pressure is 10 mTorr, with an argon partial pressure of 2.5 mTorr and a nitrogen partial pressure of 7.5 mTorr. The magnetron plasma is turned on at 500W for 1 minute. At this point, a GaN buffer layer is formed on the sapphire wafer as represented by, for example, intermediate layer **16** in Figure 1. The temperature is then increased to 1000 °C in 5 minutes and held for 10 minutes. A voltage of 100V is applied to the containment shield described hereinabove, and the containment magnets (also described hereinabove) are turned on. The magnetron plasma is ignited

and set to a power of 10kW. The plasma supplied by the injector assembly is ignited and set to a power of 5kW. The system is held in this configuration for 50 hours. The plasma is then turned off and the heater is ramped to 25 °C in 5 hours. During these stages, a single-crystal GaN boule is formed on the buffer wafer as represented by, for example, layer **32** in Figure 3. The gas flow is stopped after the crystal has cooled to room temperature. The GaN crystal boule is then removed from the chamber. The GaN boule on the sapphire is 30 mm thick and 2 inches in diameter.

One or more device-ready substrates can then be prepared from the GaN boule. The GaN boule is cut using a known technique such as, for example, by using an inside diameter wafer saw, thereby producing a GaN wafer. The wafer has a thickness of approximately 500 μm and a diameter of approximately 2 inches. The GaN wafer is then chemically or mechanically polished by known techniques. The polishing step is followed by a dry etching procedure to produce a surface on the GaN wafer receptive to a thin film of GaN. An epitaxial layer of GaN is then deposited on the prepared surface of the GaN wafer to a thickness of approximately 1 to 2 microns by an appropriate process such as, for example, sputtering, MBE, MOCVD, or HVPE. Various devices, components, and/or additional layers can then be formed on the prepared GaN substrate.

It will be understood that various details of the invention may be changed without departing from the scope of the invention. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation—the invention being defined by the claims.